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ORIGINAL ARTICLE

Spectroscopic and morphological investigation of chemically treated cellulose nanowhiskers (CNW) prepared from cotton sliver

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Abstract Cellulose nanowhiskers were prepared from cotton sliver and chemically treated with acylating agents. FTIR spectroscopy and scanning electron microscopy were used to study the morphological changes after each chemical treatment when reinforced in unsaturated polyester resin.

Keywords Cellulose nanowhisker · Cotton sliver · Scanning electron microscopy

Introduction

Cellulose—a biopolymer present most abundantly on Earth. The specific properties of cellulose make it important for the development of environmental friendly, biocompatible, and functional composites, despite its traditional and massive use in papermaking and cotton textiles (Goncalves et al. 2009). There are different types of cellulose available for the preparation of nanocomposites, namely, vegetable cellulose (VC), bacterial cellulose (BC) and nanofibrillated cellulose (NFC). It is known that regardless of similar chemistry and molecular structure, each kind of cellulose shows differences in morphology and mechanical behavior. For example, BC and NFC are composed of fibers with nanoscale dimensions as compared to VC, which improve the mechanical properties of nanocomposite materials (Martins et al. 2012).

NFC can be used as reinforcing agents in polymeric nanocomposites (Dong et al. 2012) and it is proved that properties of nanocomposites can be tailored as a function of the size, shape, and particle size distribution of the nanofillers as well as by interactions and adhering with matrix of composites. The low compatibility of cellulose in hydrophobic polymeric matrix decreases the interaction with matrix. For this reason, cellulose is chemically modified before use as reinforcing agents in matrix of low polarity. There are number of chemical treatments of cellulose related to fiber treatment (Siqueira et al. 2010); however, only few and recent papers have been published on nanoscale cellulose treatment due to recent development of such materials and their important differences in specific area compared to cellulose fibers. The surface modification of cellulose nanocrystals has been achieved using different grafting agents such as isocyanates, anhydrides (Nair et al. 2003), chlorosilanes (Goussé et al. 2002, 2004) or silanes (Grunert and Winter 2002; Lu et al. 2008). The surface chemical modification of cellulose whiskers prepared from *Halocynthia roretzi* with different silylating agents such as isopropyldimethylchlorosilane (IPDM-SiCl), *n*-butylmethylchlorosilane (BDMSiCl), *n*-octyldimethylchlorosilane (ODMSiCl) and *n*-dodecyldimethylchlorosilane (DDM-SiCl) was studied (Goussé et al. 2002). It was observed that cellulose modified with silylating agent could be dispersed in organic solvents of medium polarity. These surface chemical modifications changed the hydrophilic character

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of NFC to hydrophobic without affecting their crystalline structure.

In present study, cellulose nanowhiskers (CNW) extracted from cotton sliver via controlled acid hydrolysis and were chemically treated with acylating agents—benzoyl chloride and decanoyl chloride. The effect of these chemical treatments on the structure and morphology was studied using FTIR and SEM.

Experimental

Synthesis and purification of nanowhiskers

Combed sliver of cotton was broken into small segments of <1 cm and then soaked into 55 % H_2SO_4 at room temperature. The resulting mixture was then heated at 45 °C for 8 h with vigorous stirring. After that, a thick paste was obtained which was poured into cold-deionized water with stirring. The supernatant was decanted, and resultant material was washed with deionized water and with 2 % solution of NaOH to neutralize the excess acid. The pH was maintained at 6 in this step. The aqueous solution of hydrolyzed cellulose was obtained, which was subjected to freeze drying to get dry cellulose nanowhiskers.

Chemical modification of nanowhiskers

Cellulose nanowhiskers were suspended in pyridine for 2 h with stirring. The excess pyridine was removed in fuming hood. The nanowhiskers were then suspended in benzoyl chloride and decanoyl chloride with continuous stirring for next 2 h. The CNW were then washed with ethanol to remove any excess reagent.

Surface morphological studies

A suspension (0.03 %) of nanowhisker in acetone was prepared and incorporated in unsaturated polyester resin matrix-containing methyl ethyl ketone peroxide (MEKP) as initiator and promoter system containing ascorbic acid complex of cobalt (Fatima et al. 2012). Treated and untreated CNW were reinforced and cured at room temperature to avoid any deteriorated thermal impact on nanowhiskers. The compatibility, morphology and interaction of CNW with UPR were investigated. The IR spectra of the samples in KBr tablets were obtained using a Bruker FS-88 IR Fourier spectrometer. Changes in morphology were analyzed by scanning electron microscope (SEM) model # 6380A JEOL (Japan). The samples were first coated with gold in autocoater model # JFC-1500 JEOL (Japan).

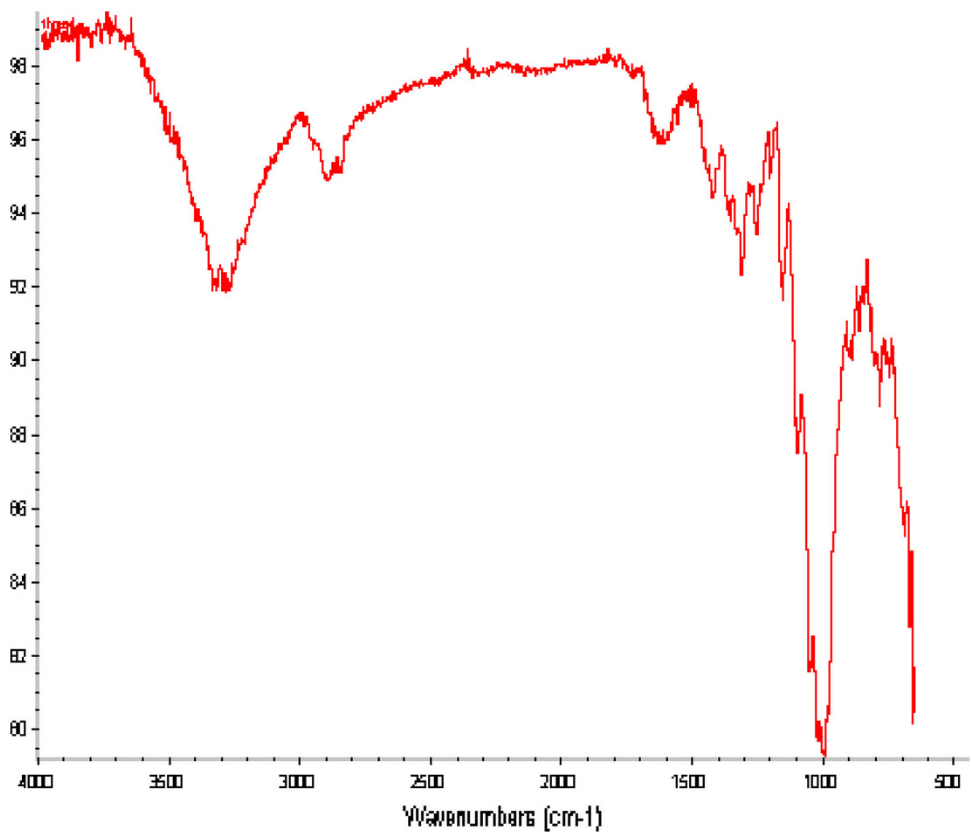

Fig. 1 IR spectra of cellulose cotton sliver

Results and discussion

Nanodimension particles from cellulose can be prepared by the partial hydrolysis with strong acid. There are number of conditions, which can control the shape and dimension of the particles. The important conditions are temperature and time of reaction. In present study, we apply a simple approach to prepare nanowhiskers from cotton sliver. The reaction was carried out at room temperature without any stirring so that acid can hydrolyze the part of fiber, which is amorphous in nature. We selected the cotton sliver, which is a combination of number of aligned fibers with amorphous region present at equal distance along the axis of fiber. Raw cotton after removal of short and immature fibers is transformed into sliver—a collection of fibers with uniform fiber. Figure 1 shows the IR spectra of cellulose

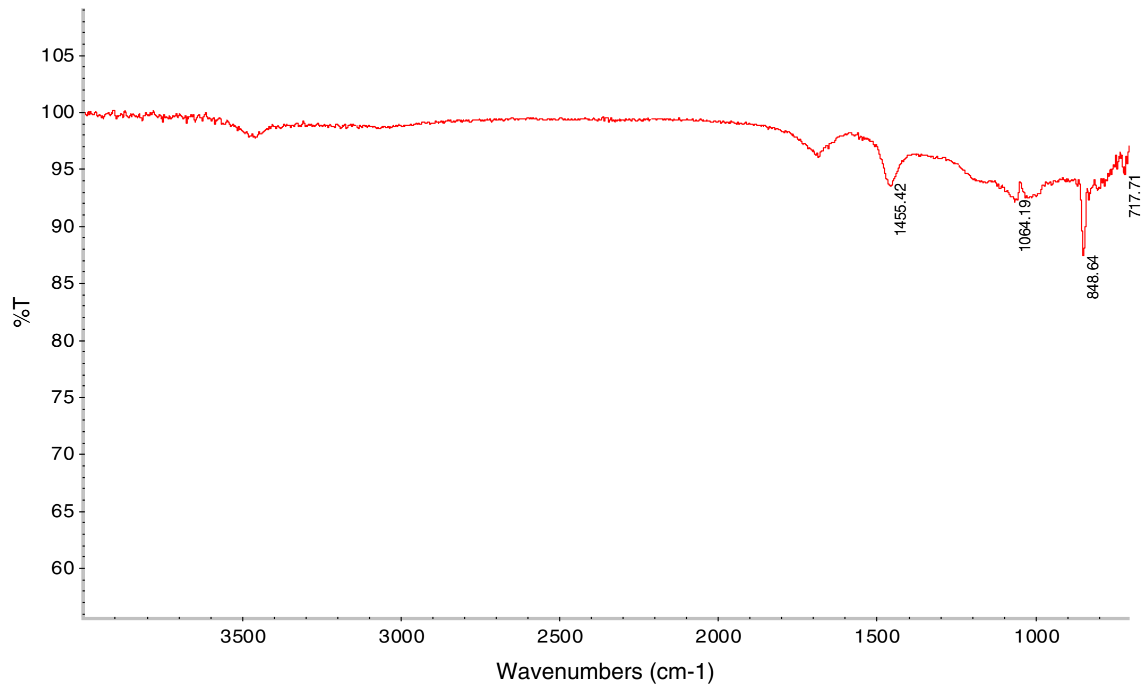

Fig. 2 IR spectra of CNW

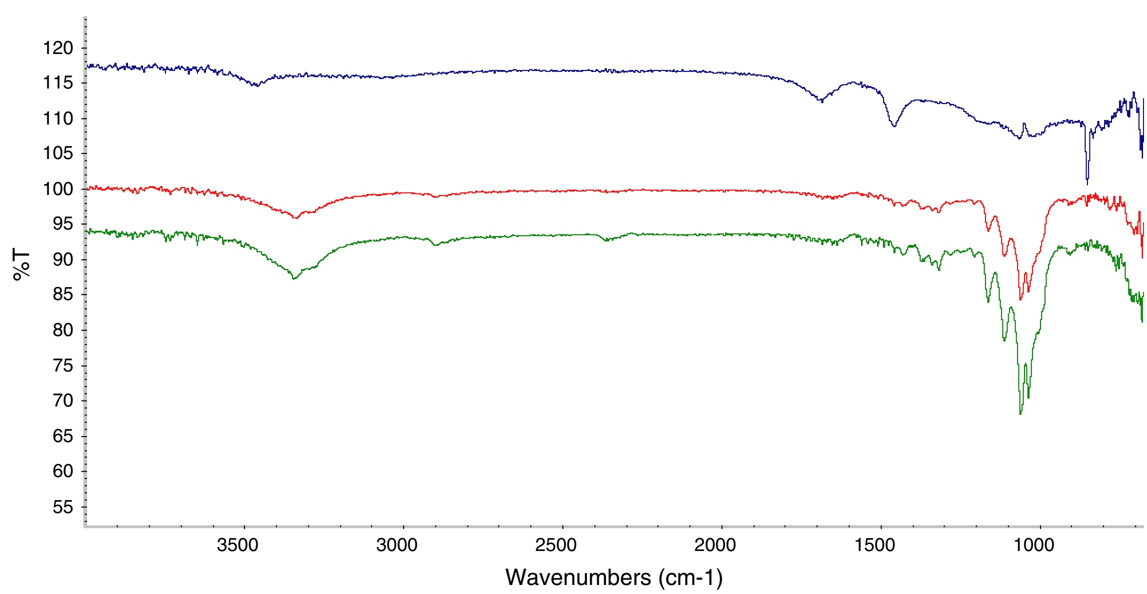

Fig. 3 IR spectrum of CNW, Bz-CNW, DC-CNW

cotton sliver. Cellulose of vegetable origin can be characterized by two absorption bands: one in the area of wavelength 3,000–3,700 cm^{-1} due to free –OH groups, and hydrogen bonding, and another at 2,900 cm^{-1} due to CH_2 and CH groups of cellulose polymer. The absorption peak at 2,900 cm^{-1} is symmetrical for pure cellulose (Shamolina 2013).

A drastic change in the peaks of IR spectrum of nanowhiskers was observed (Fig. 2). These changes in peaks are due to chemical treatment of cellulose to prepare nanowhiskers. The chemical treatment causes a breakdown of amorphous part of the fiber (Ander et al. 2008), hence increases the crystallinity index of the resultant cellulose whiskers.

Cellulose treated with benzoyl chloride and decanoyl chloride produces some characteristics bands. The band produced in the region from 950 to 1,700 cm^{-1} confirms the changes accompanied with benzoylation and decanoylation. The characteristics bands can be observed in Fig. 3.

Table 1 Crystallinity index of the cellulose, CNW and treated CNW

Sample	Crystallinity index %
Raw cellulose sliver	57.14
CNW	66.66
Bz-CNW	66.66
Dc-CNW	66.66

Each sample for FTIR spectroscopy was prepared with similar and standard conditions, which enabled an index of crystallinity of the nanowhiskers to be evaluated with the help of spectral peaks. The crystallinity index *Ic* is determined as a ratio of intensities of absorption bands at 1,372 and 2,900 cm^{-1}, I_{1372} and I_{2900}, respectively (Shamolina 2013).

Table 1 represents the results of the measurement of crystallinity index of treated and untreated CNW calculated using FTIR spectra.

Crystallinity index (C.I) of CNW is more than the starting material, which confirmed the removal of amorphous part in hydrolysis reaction. C.I of both treated CNW is similar, which shows that chemical modification of CNW is not affecting the C.I.

Surface morphology, compatibility and adhering of CNW in resin

The chemical modification of CNW is not changing the CI of the cellulose, but the impact of surface morphology and adhering in resin matrix is very interesting, which was studied by scanning electron microscopy (SEM) and FTIR spectroscopy. Cellulose is very hydrophobic in nature, hence compatibility with polar resin is a big drawback. In case of unsaturated polyester resin, which is a thick liquid, it is quite challenging to make cellulose more compatible. To overcome this problem, generally acylation is carried

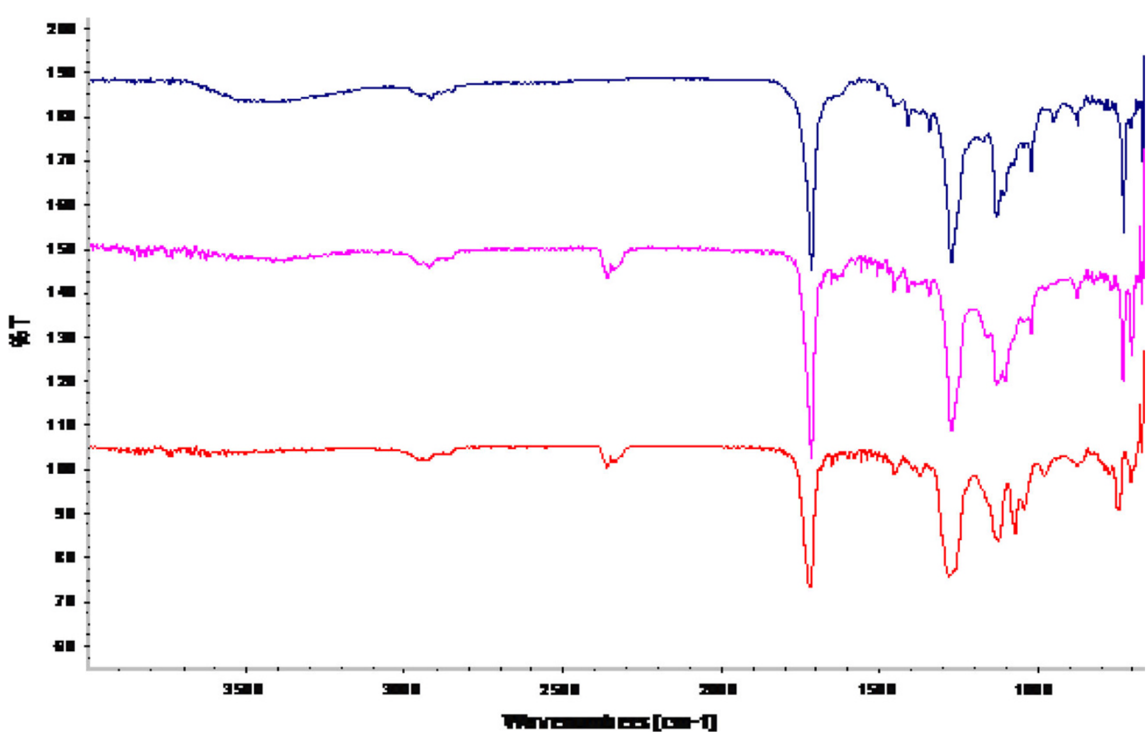

Fig. 4 FTIR spectrum of CNW (*top*), Bz-CNW (*middle*) and Dc-CNW (*bottom*)

out which makes the cellulose less hydrophobic and as a result computability increases. In present study, we carried out acylation using benzoyl chloride and decanoyl chloride to investigate compatibility and adhering. As expected, acylating has increased the compatibility of CNW in unsaturated polyester resin. Figure 4 depicts the results of compatibility of treated and untreated CNW reinforced in UPR. The characteristic peak of –OH group with low intensity can be observed at 3,550 cm^{-1} in top spectrum whereas this peak is not present in other spectra. This disappearance of peak confirmed the compatibility of treated CNW. No difference in the peak pattern is observed which shows similar compatibility of both treated CNW.

To observe the adhering capacity of CNW after each acylation, SEM was used. Breaking pattern of composite reinforced with CNW under heavy load was analyzed to observe adhering within resin. Figures 5, 6 and 7 demonstrate the adhering capacity prior and after chemical treatment of CNW. It can be seen that untreated CNW are less adhered with matrix resin as compare to treated CNW. This result is due to the increase in the hydrophobicity of CNW after the attachment of benzoyl group and decanoyl groups. These results are in agreement with previously reported publication (Mishra et al. 2003).

It can be observed from SEM images (Figs. 6, 7) that Bz-CNW is more adhered than Dc-CNW. This result is contradicted as expected with acylating agent with ten carbons chain. The hydrophobicity of ten carbon chain-acylating agent is more than benzoyl-acylating agent. The possible reason for this behavior was analyzed in surface morphology studies. Figure 8 shows the surface morphological changes after acylation via decanoyl chloride. It can be seen in SEM image that a sort of wavy surface is formed, which is due to long chain of hydrocarbon which is also responsible for less adhering despite high hydrophobicity.

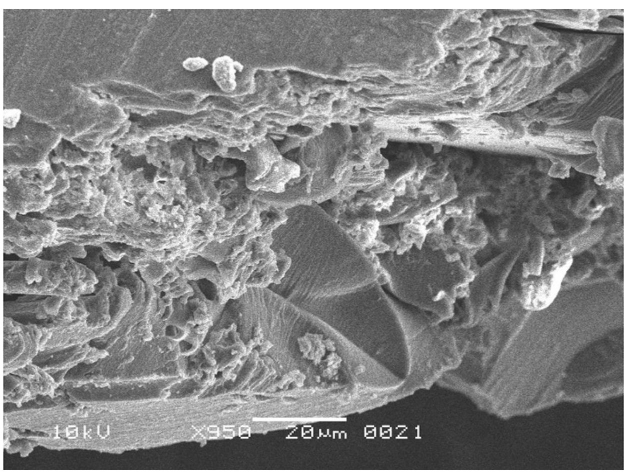

Fig. 5 Untreated CNW

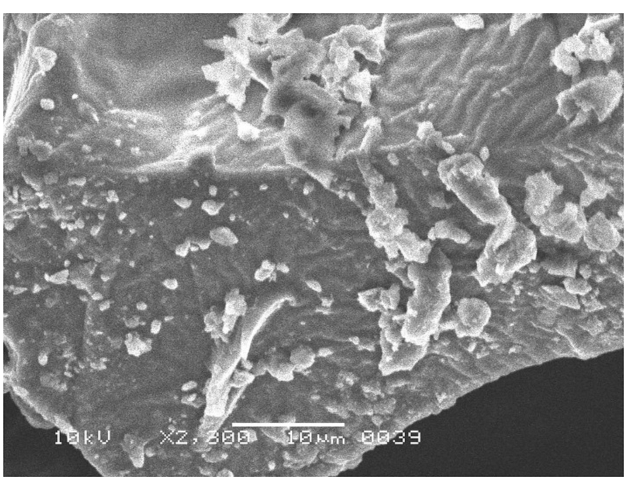

Fig. 6 Bz-CNW (benzoyl chloride treated)

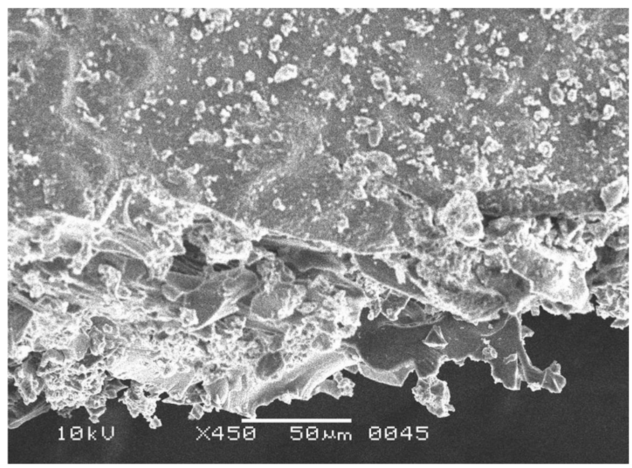

Fig. 7 Dc-CNW (decanoyl chloride treated)

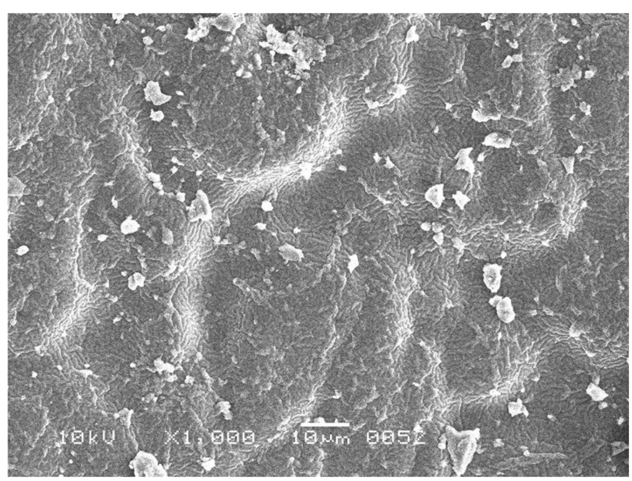

Fig. 8 A wavy surface after acylation with decanoyl chloride

Conclusion

Cellulose nanowhiskers were successfully prepared and were treated with benzoyl chloride and decanoyl chloride with an aim to increase the adhering capacity with resin matrix. Analysis of IR spectra and SEM images of CNW after these chemical treatments showed that acylation can increase the adhering capacity of CNW with resin matrix. On the other hand, long chain of carbon-acylating agent causes some sort of wavy surface of the composite, which can decrease the adhering and the strength of composites due to unevenness.

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